2766 *J. Chem. Eng. Data* **2008,** *53,* 2766–2769

Conductance and Solvation Behavior of Quinolinium Dichromate in Binary Mixtures of Water with *N*,*N*-Dimethyl Formamide

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Conductance of quinolinium dichromate has been measured in water and *N*,*N*-dimethyl formamide mixtures over the complete compositional range. The limiting molar conductance Λ_o and the association constant of the ion pair, K_A, have been computed using the Shedlovsky equation. Λ_o increases with an increase in the proportion of water in the solvent mixture. The Kraus−Bray equation has also been used to correlate the limiting molar conductance data, and the dissociation constant of the ion pair, K_C, has been computed. The results have been discussed in terms of ion−solvent interactions.

Introduction

The conductance behavior of many electrolytes in mixed solvent systems is reported to be influenced by a number of factors like density, viscosity, dielectric constant of the medium, ion−solvent interactions, and solvent−solvent interactions. Ion−solvent interactions stabilize the ion by solvating it. Though the literature is replete with such types of information,[1−10] similar information on quinolinium dichromate is lacking. This is a stable oxidant which was prepared and analyzed by Balasubramanian and co-workers.[11] It was also used as an oxidant in the kinetic studies of oxidation of different functional groupes.[12−15] In the present communication, the authors report their observations on the conductance behavior of quinolinium dichromate in binary solvent mixtures of *N*,*N*-dimethyl formamide and water.

Experimental Section

Materials. Deionized water was distilled and used. A spectroscopic grade sample of *N*,*N*-dimethyl formamide was purchased from Sd-fine Chemicals Ltd., Bombay. Quinolinium dichromate was prepared as reported in the literature.[11] A stock solution of this reagent was prepared by dissolving a known weight of the sample in water and standardizing by an iodometric method. A conductivity bridge (ELICO model-180) equipped with a glass conductivity cell of cell constant 1.103 cm^{-1} was used to measure the conductance of the solution. Temperature was maintained constant in the range (283 to 313) K using a thermostat. To maintain the temperature below room temperature, an ice bath equipped with a mechanical stirrer was used.

Measurements. The solution of quinolinium dichromate was diluted to different concentrations using different volumes of solvent/solvent mixture, and the conductance values were measured over the temperature range (283 to 313) K. From these values, the solvent conductance was subtracted, and molar conductance values Λ were evaluated at different compositions of water and *N*,*N*-dimethyl formamide mixtures in the range from (0 to 100) % (v/v).

The molar conductance (Λ) values thus determined are analyzed using the Kraus−Bray equation[17] (eq 1) and the Shedlovsky equation[17] (eq 2)

$$\frac{1}{\Lambda}=\frac{\Lambda C}{K_C\Lambda_o^2}+\frac{1}{\Lambda_o} \tag{1}$$

$$\frac{1}{S\Lambda}=\frac{Sf_{\pm}^2K_AC\Lambda}{\Lambda_o^2}+\frac{1}{\Lambda_o} \tag{2}$$

Λ is the molar conductance at concentration C; Λ_o is the limiting molar conductance; K_A is the association constant of the ion pair; K_C is the dissociation constant; $f_{\pm}$ is the mean ionic activity coefficient; and S is a factor given by

$$S=\left[\frac{\beta\sqrt{C\Lambda}}{4\Lambda^{03/2}}+\sqrt{1+\frac{\beta^2C\Lambda}{4\Lambda^{03}}}\right]^2 \tag{3}$$

$$\log f_{\pm}\left[\frac{-1.8246\cdot10^6(C\alpha)^{1/2}/(\varepsilon T)^{3/2}}{1+50.24\cdot10^8R(C\alpha)^{1/2}(\varepsilon T)^{1/2}}\right] \tag{4}$$

$$\alpha=\frac{S\Lambda}{\Lambda^0} \tag{5}$$

$$\beta=\frac{8.20\cdot10^5\Lambda^0}{(\varepsilon T)^{3/2}}+\frac{82.5}{\eta(\varepsilon T)^{1/2}} \tag{6}$$

where R is the ion-size parameter which is equal to the Bjerrum critical distance q given by

$$R=q=\frac{e^2}{2\varepsilon kT} \tag{7}$$

k is the Boltzmann's constant, and T is the temperature in Kelvin. S is calculated using Λ_o obtained from the Onsager model. The least-squares analysis of the data (Λ and C) using the above two equations (eqs 1, 2) is satisfactory with a linear correlation coefficient in the range 0.95 to 0.97.

Dichromate $Cr_2O_7^{-2}$ in the aqueous solution in the concentration range used in the present study exists in the monomeric form[16] as CrO_4^{-2} and ionizes as $HCrO^-_4$. Therefore, the conductivity equations applicable to 1:1 electrolytes are used.

Results and Discussion

The limiting molar conductance values Λ_o obtained using the two equations (eq 1 and eq 2) are presented in Table 1. These values increase with an increase in temperature as expected. The Λ_o values also depend on the composition of

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10.1021/je800328q CCC: $40.75

Table 1. Limiting Molar Conductance Values in mho $cm^2 \cdot mol^{-1}$ of Quinolinium Dichromate in Water + *N,N*-Dimethyl Formamide[a]

	0 % water		20 % water		40 % water		60 % water		80 % water		100 % water	
T (K)	1	2	1	2	1	2	1	2	1	2	1	2
283	26.08	26.16	65.24	67.06	60.58	61.13	86.13	85.57	116.36	114.84	121.66	122.27
293	48.22	48.37	75.29	82.42	88.18	87.73	117.81	118.26	136.20	138.88	143.89	138.02
303	55.36	54.99	82.42	80.19	107.96	107.99	133.57	132.03	139.82	139.60	154.66	154.93
313	73.07	73.08	97.00	96.75	135.65	136.24	147.07	147.07	172.59	174.60	196.67	196.40

[a] 1 = Kraus−Bray model. 2 = Shedlovsky model.

Table 2. K_A and K_C Values of Quinolinium Dichromate in Water + *N,N*-Dimethyl Formamide Mixtures[a]

	0 % water		20 % water		40 % water		60 % water		80 % water		100 % water	
T (K)	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C	K_A	K_C
283	81.97	0.01	77.34	0.14	12.41	0.08	28.30	0.02	34.14	0.04	54.67	0.02
293	27.89	0.04	66.22	0.20	15.21	0.07	22.69	0.04	20.42	0.05	70.07	0.01
303	23.50	0.04	32.55	0.20	12.63	0.08	15.78	0.06	11.22	0.09	28.24	0.02
313	28.90	0.03	6.11	0.04	10.80	0.09	8.33	0.11	6.97	0.15	21.89	0.05

[a] K_A = Association constant from the Shedlovsky equation. K_C = Dissociation constant from the Kraus−Bray equation.

Table 3. Computed Values of E_a ($kJ \cdot mol^{-1}$) and ΔH_a ($kJ \cdot mol^{-1}$) for Quinolinium Dichromate under Varying Compositions (v/v) of Water + *N,N*-Dimethyl Formamide Mixtures at All Temperatures

	0 % water	20 % water	40 % water	60 % water	80 % water	100 % water
E_a	26.69	9.84	21.70	14.42	10.49	12.69
ΔH_a	13.533	63.644	12.90	12.82	39.83	45.10

the binary solvent mixture. Addition of *N,N*-dimethyl formamide to water decreases the Λ_o value. From the slopes obtained by the linear least-squares analysis using the Kraus−Bray and Shedlovsky models, the dissociation constant K_C and the association constant K_A of the ion pair have been evaluated and are presented in Table 2. These K_A values do not change regularly with the composition of the solvent mixture.

Conductivity increases with an increase in temperature. It is supposed that this variation has to follow the Arrhenius relation, so the energies of activation of the conducting process are obtained from the Arrhenius relationship, i.e.

$$\Lambda_0 = A e^{-E_a/RT}$$

where A is a constant. E_a is the activation energy of the conducting process; R is the gas constant; and T is the temperature in Kelvin. The calculated E_a values are presented in Table 3. These values are lower in 20 % (v/v) water−*N,N*-dimethyl formamide than in other solvent systems.

Thermodynamic Parameters. The K_A value is used to compute thermodynamic parameters, namely, the change in enthalpy (ΔH_a), change in entropy (ΔS_a), and change in free energy (ΔG_a) accompanied by the association process. The observed association constants, K_A, in general, are found to decrease with an increase in temperature. A plot of log K_A versus $1/T$ was linear with a positive slope. A positive ΔH_a means that endothermic interaction exists between the ions. There appears to be no regular variation in the ΔH_a values due to the change in the composition of the solvent. The free energy change accompanied by the ion pair formation (ΔG_a) is computed using the relation $\Delta G_a = -RT \ln K_A$, calculated at all temperatures and tabulated in Table 4. The entropy change accompanying the association process (ΔS_a) is computed using the relation $\Delta G_a = \Delta H_a - T\Delta S_a$. These values are presented in Table 5.

The differential free energy change in different solvents is computed using the equations

$$\Delta G_t = -RT \ln(\mathrm{w}K_A/\mathrm{s}K_A) \tag{8}$$

and

$$\Delta G_t = \Delta G_t(\mathrm{s}) - \Delta G_t(\mathrm{w}) \tag{9}$$

where wK_A and sK_A are the association constant of the ion pair in water and in the solvent mixture, respectively. ΔG_t is the free energy accompanied by the addition of different amounts of *N,N*-dimethyl formamide to water. The magnitude of ΔG_t depends on the relative magnitude of stabilization of the ion pair and is presented in Table 4.

In solution, the ion pair is solvated, and it is stabilized due to solvation. The change in the free energy accompanied

Table 4. Computed Change in Free Energy (ΔG_a) and Transfer (ΔG_t) for Quinolinium Dichromate in Water + *N,N*-Dimethyl Formamide Mixtures at All Temperatures in $kJ \cdot mol^{-1}$

	0 % water		20 % water		40 % water		60 % water		80 % water		100 % water	
T (K)	ΔG_a	ΔG_t	ΔG_a	ΔG_t	ΔG_a	ΔG_t	ΔG_a	ΔG_t	ΔG_a	ΔG_t	ΔG_a	ΔG_t
283	−4.94	−4.47	−10.22	0.81	−5.92	−3.50	−7.86	−1.55	−8.27	−1.14	−9.41	–
293	−8.07	−2.24	−10.09	−0.17	−6.61	−2.92	−7.62	−2.74	−7.34	−3.24	−10.36	–
303	−7.99	−0.41	−7.99	0.37	−6.37	−2.03	−6.94	−1.46	−6.08	−2.32	−8.40	–
313	−8.74	0.72	−4.55	−3.32	−6.18	−1.84	−5.51	−2.50	−5.03	−2.99	−7.76	–

Table 5. Computed Change in Entropy (ΔS_a) and (ΔS_t) for Quinolinium Dichromate in Water + *N,N*-Dimethyl Formamide Mixtures at All Temperatures $J \cdot K^{-1} \cdot mol^{-1}$

	0 % water		20 % water		40 % water		60 % water		80 % water		100 % water	
T (K)	ΔS_a	ΔS_t	ΔS_a	ΔS_t	ΔS_a	ΔS_t	ΔS_a	ΔS_t	ΔS_a	ΔS_t	ΔS_a	ΔS_t
283	84.00	64.00	261.00	222.00	67.00	58.00	133.00	111.00	170.00	145.00	192.30	–
293	74.00	54.00	252.00	218.00	66.00	54.00	128.00	111.00	160.00	147.00	189.00	–
303	71.00	46.00	236.00	209.00	64.00	49.00	121.00	103.00	152.00	139.00	460.00	–
313	71.00	41.00	218.00	204.00	61.00	47.00	113.00	103.00	140.00	137.00	169.00	–

Table 6. Computed Change in Free Energy of Solvation ($\Delta G_{i\text{-}s}$) for Quinolinium Dichromate in Water + *N,N*-Dimethyl Formamide at Different Temperatures in $kJ \cdot mol^{-1}$

T (K)	0 % water	20 % water	40 % water	60 % water	80 % water	100 % water
283	−9.33	−7.69	−7.02	−5.77	−4.75	−3.30
293	−7.50	−8.71	−7.33	−6.07	−4.85	−3.40
303	−6.27	−8.52	−7.49	−6.34	−4.93	−3.93
313	−5.78	−8.69	−6.5	−6.78	−5.23	−3.75

Table 7. Corrected Stoke's Radius in Λ^0 of the Species of Quinolinium Dichromate under Varying Compositions (v/v) of Water + *N,N*-Dimethyl Formamide at Different Temperatures

T (K)	0 % water	20 % water	40 % water	60 % water	80 % water	100 % water
283	3.86	1.90	1.75	1.83	1.96	2.50
293	2.53	1.77	1.75	1.81	1.99	2.55
303	3.13	1.87	1.78	1.84	2.07	2.30
313	3.61	1.95	2.18	1.89	2.04	2.53

Table 8. Walden Product ($\Lambda^0\eta^0$,$S\ cm^{-1} \cdot kg \cdot m^{-1} \cdot s^{-1}$) of the Conducting Molecular Species of Quinolinium Dichromate in Water + *N,N*-Dimethyl Formamide Mixtures

T (K)	0 % water	20 % water	40 % water	60 % water	80 % water	100 % water
283	0.314	2.15	2.57	2.65	2.41	1.59
293	0.43	1.90	2.37	2.60	2.08	1.38
303	0.39	1.28	2.05	2.11	1.68	1.24
313	0.37	1.45	2.04	1.77	1.57	1.80

Table 9. Solvation Number Values for Ion Pair Formation of Quinolinium Dichromate in Water + *N,N*-Dimethyl Formamide Mixtures at Different Temperature

T (K)	0 % water	20 % water	40 % water	60 % water	80 % water	100 % water
283	0.57	1.15	1.65	1.76	1.82	1.64
293	1.71	1.86	2.79	2.59	2.79	2.77
303	1.54	2.04	2.82	2.61	2.82	2.94
313	1.78	2.10	3.17	2.72	3.17	3.30

by this solvation process $\Delta G_{i\text{-}s}$ is calculated using the Born equation,[17] at each composition of the solvent. These values determined in the temperature range (283 to 313) K are tabulated in Table 5. These are all negative and decrease in magnitude gradually with an increase in water content of the solvent mixture. $\Delta G_{i\text{-}s}$ is a measure of the stability of the solvated system, and the larger the negative value, the higher the stability of the species will be. The data presented in Table 6 suggest that the solvated species is more stable in (80 to 100) % (v/v) *N,N*-dimethyl formamide mixtures.

Solvation Number. The solvation number (S_n) which is the number of solvent molecules in the solvent sheath around the species is calculated from the effect of the dielectric constant ($\in$) on Λ_o based on the equation

$$\log \Lambda_0 = \log \Lambda_0^1 - \frac{Z_A Z_B e^2}{\in d_{AB} k_B T} \tag{10}$$

Z_Ae and Z_Be are the ionic charges; k_B is the Boltzmann constant; *T* is the temperature; and d_{AB} is the distance between the centers of the two ions. A plot of log Λ_o against 1/$\in$ is linear with negative slope, from which d_{AB} is computed. S_n is computed using the relation

$$S_n = \frac{d_{AB} - r_i}{r_{solvent}} \tag{11}$$

where r_i is the Stokes radius of the ion calculated using Stoke's radius equation.[18]

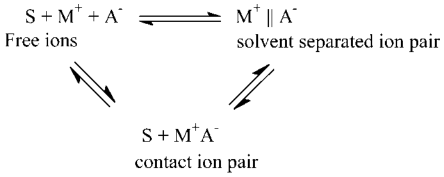
$$r_i = \frac{0.820|Z|}{\Lambda_o \eta_o} + 0.0103 \in + r_y \tag{12}$$

where $r_y = 0.85\Lambda^0$ for dipolar unassociated solvents and $1.13\Lambda^0$ for protic and associated solvents. These r_i values are tabulated in Table 7.

$\Lambda_0\eta_0$ is the Walden product and is the product of limiting conductance of the electrolyte and the viscosity[19](η_0) of the solvent. The Walden product values calculated at all temperatures and % compositions of water and *N,N*-dimethyl formamide are shown in Table 8.

The solvation number thus determined for the ion pair increases with an increase in temperature at all compositions of the solvent mixture. At a given temperature, addition of water to *N,N*-dimethyl fomamide slightly increases the solvation number. These values are represented in Table 9.

The process of ion pair formation may be represented as



The variable solvation number indicates that the ion pair is solvated to different extents depending on the composition of the solvent which reflects variable ion−solvent interactions.

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Received for review May 8, 2008. Accepted October 19, 2008.

JE800328Q